

1,017,244



PATENT SPECIFICATION

NO DRAWINGS

1,017,244

Date of Application and filing Complete Specification: July 26, 1963.

No. 29777/63.

Application made in Germany (No. F37435 IVd/39b) on July 27, 1962.

Complete Specification Published: Jan. 19, 1966.

© Crown Copyright 1966.

Index at acceptance:—C3 R(32C8, 32D1, 32D2, 32D4, 32D6, 32E1, 32E2, 32E5, 32E7, 32E8);
C3 P(11C13A, 11D5, 11K11, 11T2D, 11T2X)

Int. Cl.:—C 08 g

COMPLETE SPECIFICATION

The Inventors of this invention in the sense of being the devisers thereof within the meaning of Section 16 of the Patents Act, 1949 are:—Kuno Wagner Am Kiesberg 8, Leverkusen, Germany, Harry Rohr, Kartauser Hof 35—37, Köln, Germany, Both are of German Nationality.

Thermoplastically Deformable Compositions

We, FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT of Leverkusen-Bayerwerk, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to thermoplastically deformable compositions. It has now been found that difficultly soluble polyoxymethylenes of high molecular weight have the surprising property of dissolving at temperatures above 130°C. in polyurethanes of molecular weight at least 8000 and of various structures. Homogeneous mixtures of any desired concentrations of the two components are possible if the temperature is raised further and these mixtures can be used as thermoplastically deformable compositions.

The invention is consequently concerned with the modification of polyurethanes of molecular weight at least 8000 by polyoxymethylenes of high molecular weight, and *vice versa*, to form interesting thermoplastically deformable compositions. Due to the manifold possibilities of variation in structure and nature of the terminal groups of the polyoxymethylenes and polyurethanes, and furthermore due to the chemical processes taking place with the shaping at high temperature, these synthetic plastics obtained from such polyurethanes and polyoxymethylenes have properties which were not to be expected from a simple mixture of the starting materials used.

The present invention provides a thermoplastically deformable composition, which comprises a polyurethane of high molecular weight at least 8000 and a polyoxymethylene

[P-----]

of molecular weight at least 4000, the ratio of the polyurethane to the polyoxymethylene being from 5 : 95% by weight to 95 : 5% by weight.

The term "polyoxymethylene of high molecular weight" as used herein means polymers of molecular weight of at least 4000 containing a plurality of recurring $-(CH_2O)-$ groups.

It is well known that polyoxymethylenes are polymerisation products of formaldehyde or trioxane. They can contain terminal functional groups, such as hydroxyl or mercapto groups, or such groups can be stabilised by etherification or acylation, i.e. they can contain terminal ether or acyl groups.

Examples of polyoxymethylenes which can be used in the invention are homopolymers of formaldehyde and copolymers of formaldehyde or trioxane with cyclic acetals or 1,2-epoxy compound (for example with 1,3-dioxolane, ethylene oxide or propylene oxide). The co-monomers which are polymerised with the formaldehyde or trioxane are generally used in very small amounts, e.g. about 1% by weight. The polyoxymethylenes generally have an intrinsic viscosity of 0.1—5, measured in butyrolactone in a 0.5% solution at 150°C. and a molecular weight of from 4000—250,000. The most preferable polyoxymethylenes are especially polymers which are stabilised at their terminal groups by acylation or etherification and have an intrinsic viscosity of 0.2—1.5. From this group of terminal-stabilized polymers, the greatest interest is attributed to polyoxymethylenes of high molecular weight which comprise true alcoholic OH-groups or mercapto groups on their terminal groups. As a result, these groups are in a position to react in a chain extending or branching reaction with polyurethanes

BEST AVAILABLE COPY

which still contain free NCO-groups or masked isocyanates as incorporated groups. Such polyoxymethylenes containing alcoholic terminal OH-groups can, by analogy to
5 known processes, be produced by etherification reactions from ω , ω^1 -dihydroxy-polyoxymethylenes and bifunctional alcohols with relatively strong degradation of the polyoxymethylenes, and also by reacting the ω , ω^1 -dihydroxy-
10 polyoxymethylenes with glycol formal, polyacetals of molecular weight 400 to 3000 obtained from ethylene glycol and formaldehyde, mercaptoethanol, ethylene oxide or propylene oxide in the presence of acid catalysts.
15 One preferred group of polyoxymethylenes can be produced without degradation by a direct method and by the procedure disclosed in U.S.A. Patent Specification No. 3,027,352 by copolymerising trioxane with 1,3-dioxolane or ethylene oxide or its derivatives (as co-
20 monomers) and depolymerising the polymers as far as the two terminal co-monomeric units. This group of polyoxymethylenes of high molecular weight can be incorporated quantitatively in the processing of the thermo-
25 plastically deformable compositions according to the invention and, by suitably choosing the polyurethanes containing free NCO-groups, polyoxymethylene units of a highly crystalline nature can be grafted on to the polyurethane
30 chain segments.

Other polyoxymethylenes which can be used are polyoxymethylene diacetates and polyoxymethylene ethers such as the dimethyl
35 ether, diethyl ether and benzyl ether. They are capable of being homogeneously mixed with the polyurethanes at 100 to 180°C. Since they contain no free groups capable of reacting with NCO groups, they react with
40 the polyurethanes only at such temperatures during the forming or moulding process due to the progress of the cracking reactions. In fact, they react with the NH-groups, amino groups, urea groups or incorporated components which can easily be cross-linked with
45 formaldehyde (such as ethoxylated toluidine) and lead to an increase in the degree of cross-linking of moulded elements produced from the compositions. This becomes apparent by a reduction in the permanent elongation
50 by comparison with the pure polyurethanes, a fact which is often desirable.

The polyurethanes can be obtained by the isocyanate polyaddition process. The structure thereof, depending on various types of
55 polyisocyanates, polyhydroxyl compounds with molecular weights of 500—4000 and, if desired, chain extenders (such as monomeric polyhydric alcohols, polyamines, water, hydrazines, ethoxylated ureas, ethoxylated poly-
60 phenols and aromatic polyamines) is known to be readily controllable. Due to the nature of the reaction components, the quantities thereof, the temperature control and whether catalysed or uncatalysed chain extending or

branching reactions occur, it is possible for the structure and nature of the terminal groups of the polyaddition products of high molecular weight to be varied to a large degree.

The products preferably are polyurethanes of high molecular weight which are produced from (a) polyesters, polyethers (such as polyethylene glycol ethers, polypropylene glycol ethers or polybutylene glycol ethers) polyester amides, polythioethers or polyacetals
75 with a molecular weight from 500—4000 or their graft derivatives with for example acrylonitrile, vinyl acetate or vinyl chloride and (b) aromatic or aliphatic polyisocyanates and (c) chain extenders such as glycols or water.
80 They should preferably have a relatively low degree of branching, i.e. corresponding to an intrinsic viscosity values from 0.4—2 (measured in dimethylformamide at 30°C.); their terminal groups can for example be OH—, NCO—, amino—, hydrazine— or substituted amino groups. Furthermore, such preferable polyurethanes can contain within their chains
85 uretdione rings, unsaturated polymerisable groupings or groupings which can be cross-linked with sulphur (such as residues of glycerol monoallyl ether or butene-1,4-diol, as well as residues of compounds which are available for a cross-linking reaction with
90 formaldehyde, such as ethoxylated aromatic polyphenols, bis-hydroxyethylated aniline, *m*-toluidine, xylidine, hydroxyalkylated ureas, urethanes or amides).

Where the preferred polyurethanes have a noticeable degree of branching or cross-linking, it is advantageous if the branches consist of linkages (such as allophanate and biuret branches) which can more easily be detached by heat and which can for example be formed
105 by the use of ortho-substituted polyisocyanates according to Specification No. 983174. However, also to be mentioned are polyurethanes which are prepared by the procedure disclosed in Application No. 21947/63 Serial
110 No. 1,015,340 using an excess of more than 500% of polyisocyanate, it also being possible in certain cases for unsaturated polyhydroxyl compounds and, as cross-linking agents, polymerisable monomeric vinyl com-
115 pounds, to be employed concurrently.

The thermoplastically deformable compositions according to the invention are obtained by simply mixing the polyoxymethylenes and the polyurethanes in the required proportions.
120 The mixing operation is continued until homogenisation is achieved, this requiring temperatures of 100 to 200°C. The mixing temperature depends on the actual components, their proportions and their thermoplastic behaviour. Generally speaking, temperatures
125 from 160—180°C. are used. The mixing can take place on rollers but if required can be carried out by melting together.

The mixing ratio of the components can 130

fluctuate from 5—95% by weight to 95—5% by weight. Thus, smaller quantities of polyurethanes within this range act as chemically incorporated plasticiser, which considerably increase the notch toughness of the polyoxymethylenes, though the incorporation of 20—40% by weight of polyoxymethylene into the polyurethane is also advantageous.

This is because thermoplastically deformable compositions containing about 40% by weight of polyoxymethylene are of interest because they have a maximum degree of tensile strength and breaking elongation and show excellent stability with respect to organic solvents and also show an increased resistance to swelling with respect to aromatic hydrocarbons. The increased permanent elongation of the thermoplastic polyurethane is also reduced in a favourable manner. The resistance to hydrolysis of moulded elements which can be obtained from the composition is improved, since polyurethane fragments containing amino groups formed due to ageing and hydrolysis can be converted again with traces of formaldehyde into cross-linked products of high molecular weight.

The thermoplastically deformable compositions according to the invention can also be subsequently processed under pressure for 1—40 minutes while shaping using a temperature of for example 180—220°C. They are available for all working methods which are typical for thermoplastic compositions and can for example be processed by injection moulding or by extrusion or welding to produce moulded elements, sheet structures and coatings.

In accordance with one particular embodiment, the compositions may contain polyoxymethylenes with β -hydroxyalkyl radicals and polyurethanes with free NCO-groups. These compositions may contain other polyisocyanates, more especially polyisocyanates containing uretdione, sulphur or peroxides, for example dicumyl peroxide or ditert. butyl peroxide.

Heat stabilisers, antioxidants or fillers can readily be added to the compositions according to the invention. The following Examples illustrate the invention.

EXAMPLE 1

Production of the polyoxymethylene B

250 parts by weight of trioxane were copolymerised, in 250 parts by volume of anhydrous cyclohexane, with 2.5 parts by weight of 1,3-dioxolane using 1 part by weight of boron trifluoride etherate as catalyst. The polymerisation temperature was 60—68°C and the polymerisation period was four hours. The polymer obtained was filtered off, and washed several times with acetone and dilute aqueous sodium carbonate solution, distilled water and finally with methylene chloride and dried. The dried polymer was thereafter heated *in vacuo* at 160°C. for several hours, the polymer being degraded as far as the first two terminal comonomer units and a product with terminal β -hydroxyethyl groups was obtained (loss in weight: 32% of formaldehyde split off).

Production of the polyurethane A

200 parts by weight of a polyester of adipic acid and ethylene glycol (OH-number 56) were dehydrated *in vacuo* at 110°C. and reacted with 160 parts by weight of diphenylmethane-4,4'-diisocyanate. After cooling to 100°C., 46 parts by weight of butane-1,4-diol were incorporated by stirring and the mixture which was obtained was poured on to a plate heated to 90°C. After 2 minutes, the sheet thus obtained was cooled to room temperature and thereafter granulated.

Polyurethane A was homogeneously mixed on a mixing roller (temperature 170—180°C.) with the quantities by weight of the polyoxymethylene B indicated in Table I, the said polyoxymethylene containing 1% of a polyamide of polymerised caprolactam as heat stabiliser and 0.5% of 2,6-ditert.-butyl-phenol as antioxidant.

TABLE I

No.	Parts by weight Polyoxymethylene B	Percentage by weight	Parts by weight polyurethane A	Percentage by weight
1	60	30	140	70
2	80	40	120	60
3	120	60	80	40
4	140	70	60	30
5	180	90	20	10

The thermoplastically deformable compositions according to Table I were pressed under heat and pressure to form a homogeneous pressed plate. The test elements obtained had the following mechanical properties: 5

TABLE II

Pressed plates	Notch toughness cm kp/cm ³	Bending Strength kp/cm ²	Tensile Strength kp/cm ²	Breaking elongation %	Ball indentation hardness kp/cm ²	Martens degree °C.	Vicat degree °C.
Polyoxymethylene B for comparison	4.4	975	654	54	1365—1295	70	180
Polyurethane A	— 1)	—	341	500	—	—	—
Ratio by weight							
B A	— 1)	176	410	399	163—152	—	96
30 : 70							
40 : 60	— 1)	241	476	476	258—240	—	101
60 : 40	30.7	346	376	368	470—435	36	145
70 : 30	19.4	485	398	144	700—650	48	160
90 : 10	7.5	800	530	60	1130—1070	61	168

The test elements also had a substantially reduced permanent elongation of 3—4%, as compared with the permanent elongation of polyurethane of 57%.

1) — cannot be measured because of high elasticity.

EXAMPLE 2

60 Parts by weight of polyoxymethylene containing two terminal acetate groups (C) and 60 parts by weight of polyoxymethylene containing two terminal ether groups (D) were each mixed with 140 parts by weight of polyurethane A. The polyoxymethylenes were homopolymers of formaldehyde and the intrinsic viscosities of C and D, measured in butyrolactone at 150°C. in 0.5% solution were:

C) $\eta_i = 0.81$, D) $\eta_i = 0.62$.

After shaping to form a pressed or moulded plate in accordance with the conditions of Example 1, homogeneous, blister-free test elements were obtained with the mechanical properties indicated in Table III and a good resistance to swelling with respect to different organic solvents, and advantageously also with respect to aromatic hydrocarbons.

TABLE III

	Bending strength kp/cm ²	Tensile strength kp/cm ²	Breaking elongation %	Permanent elongation cm
A+C	180	408	405	5
A+D	171	420	395	8

EXAMPLE 3

Production of polyurethane E

174 Parts by weight of toluylene diisocyanate, after dehydration at 130°C. were incorporated in 1 kg. of a glycol-adipic acid polyester (OH number 51) by stirring, heated for about 20 minutes to 120—130°C. and then 10 cc. of water were added while stirring vigorously at 100—110°C. After a few seconds, the reaction started with the evolution of CO₂. The viscous melt was poured on to metal sheets and further heated for 24 hours at 90°C. An elastic polyurethane composition was formed, which was ground in a mill to give a white powder.

Production of polyurethane F

Into 100 parts by weight of adipic acid-glycol polyester (OH-number 55) dehydrated at 130°C/12 mm.Hg., there were incorporated by stirring 50 parts by weight of dimeric toluylene-2,4 diisocyanate at a temperature below 95°C. until dissolved. After the solution had formed, 180 parts by weight of diphenyl methane-4,4'-diisocyanate were added at 90°C. and thereafter 33.5 parts by weight of butane-1,4-diol were added as chain extender. When required, the reaction temperature was kept below 95°C. by cooling. The clear melt was poured into moulds, further heated for 2½ hours at 85—95°C. and the storable polyurethane composition which could be rolled on rubber mixing rolls to give a smooth sheet was removed from the mould when cold.

80 parts by weight of polyoxymethylene B were homogeneously mixed on a mixing roll at 170—180°C. with, in each case, 120 parts by weight of the following polyurethane compositions:

- 1) Polyurethane E
- 2) Polyurethane A with the diphenylmethane-4,4'-diisocyanate replaced by phenylene-1,4-diisocyanate.
- 3) Polyurethane F
- 4) Polyurethane A, but with 9 parts by weight of butane-1,4-diol were replaced by 1.8 parts by weight of water.
- 5) Polyurethane A, but the polyester was replaced by a polythioether of thiodiglycol and triethylene glycol (70 : 30) (OH-number 56).
- 6) Polyurethane A, with replacement of 9 parts by weight of butane-1,4-diol by 19 parts by weight of bis-β-hydroxymethyl-m-toluidine.
- 7) Polyurethane A, the polyester being replaced by a polybutylene glycol ether (OH-number 56).

Under the conditions indicated in Example 1, homogeneous, blister-free moulded elements were obtained from the thermoplastically deformable compositions, these elements having a high stability and resistance to swelling with respect to organic solvents and with mechanical properties which corresponded approximately to the values in line 4 of Table II and permanent elongations of 3—8%.

WHAT WE CLAIM IS:

1. A thermoplastically deformable composition, which comprises a polyurethane of high molecular weight at least 8000 and a polyoxymethylene of molecular weight at least 4000, the ratio of the polyurethane to the polyoxymethylene being from 5 : 95% by weight to 95 : 5% by weight.
2. A composition as claimed in claim 1, wherein the polyoxymethylene is a polyoxymethylene which is stabilised by acylation or

etherification and has an intrinsic viscosity of 0.2—1.5.

3. A composition as claimed in claim 1, wherein the polyoxymethylenes have terminal alcoholic —OH or —SH groups.
- 5

4. A composition as claimed in claim 3, wherein the polyoxymethylene is a copolymer of trioxane and 1,3-dioxolane or ethylene oxide.

- 10 5. A composition as claimed in claim 3, wherein the polyoxymethylene contains terminal -hydroxyalkyl ether radicals.

6. A composition as claimed in any of the preceding claims, wherein the polyurethane contains free —NCO groups and has an intrinsic viscosity of 0.4 to 2.
- 15

7. A composition as claimed in any of claims 1 to 5, wherein the polyurethane is the reaction product of one or more polyisocyanates, a polyhydroxy compound and a chain extender.

20

8. A composition as claimed in claim 1, substantially as described with reference to any of the Examples.

ELKINGTON AND FIFE
Chartered Patent Agents,
High Holborn House, 52—54 High Holborn,
London, W.C.1.
Agents for the Applicants.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☒ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☒ **FADED TEXT OR DRAWING**
- ☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKewed/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.